

**BELLCOMM, INC.**

1100 Seventeenth Street, N.W. Washington, D.C. 20036

**SUBJECT:** Preliminary Chemical Considerations  
of Polymer Combustion - Case 320**DATE:** May 13, 1968**FROM:** M. V. DrickmanABSTRACT

A qualitative picture of the factors involved in polymer combustion, with an emphasis on chemical considerations, is presented. This includes basic definitions relating to polymers, a scheme for polymer combustion, and some differing views of the controlling factors involved in combustion.

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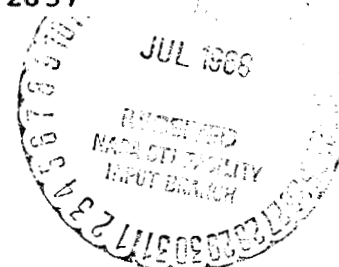
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## INTRODUCTION

As a result of the Apollo fire of January, 1967, extensive testing has been done on the flammability properties of nonmetallic components of the spacecraft. A considerable proportion of these materials are organic polymers. In addition to collecting data, there has been a concern with a theoretical approach and explanation. This memorandum presents some basic definitions concerning polymers and also gives a qualitative description of the processes involved in combustion. Later papers will deal with experimental results and a more quantitative picture of combustion and will assume a familiarity with the material presented here. It is hoped that this information will be helpful in interpreting the data.

## GENERAL BACKGROUND

## 1. Polymers

A polymer molecule is a large molecule composed of smaller primary units which are chemically bound together. These small, primary units are commonly known as monomers; the number of monomer units in the polymer is called the degree of polymerization. The degree of polymerization can be of the order of hundreds or thousands. A typical polymer molecule will consist of a long, chain-like structure having considerable freedom of motion.

Some of the common polymers are listed below:

<u>NAME</u>	<u>POLYMER REPEATING UNIT</u>
Polystyrene	$\{CH_2-\underset{\substack{  \\ C_6H_5}}{CH}}\}_n$
Polyethylene	$\{CH_2-CH_2\}_n$
Polytetrafluoro-ethylene (TEFLON)	$\{CF_2-CF_2\}_n$

<u>NAME</u>	<u>POLYMER REPEATING UNIT</u>
Polyesters	$\begin{array}{c} \text{O} \\ \parallel \\ \{(\text{CH}_2)_n - \text{C} - \text{O}\}_n \end{array}$
Polyamides (Nylon)	$\begin{array}{c} \text{H} \qquad \text{O} \\ \parallel \qquad \parallel \\ \{\text{N} - (\text{CH}_2)_n - \text{C}\}_n \end{array}$
Polyurethanes	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ [\text{O} - (\text{CH}_2)_n - \text{O} - \text{C} - \text{N} - (\text{CH}_2)_n - \text{N} - \text{C}]_n \\ \qquad \qquad \text{H} \qquad \qquad \text{H} \end{array}$

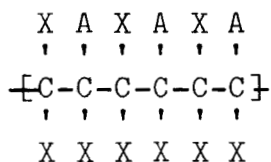
The polymers listed here are examples of homopolymers, i.e., the repeating units consist of only one monomer. It is also possible to synthesize polymers which contain more than one monomer; these are called copolymers. Further, the above polymers all contain a predominantly carbon backbone and are therefore usually referred to as organic polymers. Those which have a non-carbon backbone are sometimes called inorganic polymers.

Polymers are usually characterized as either condensation or addition polymers. This nomenclature arises from the type of reaction involved in the polymerization. A condensation polymer, e.g., nylon, arises when two monomer units react yielding a larger molecule and a small, non-reactive molecule (e.g., water). These polymers usually have molecular weights of the order of  $10^4$ . Addition polymers arise from the combination of monomers containing double bonds, e.g., ethylene ( $\text{H}_2\text{C} = \text{CH}_2$ )  $\rightarrow$  polyethylene. Polymerization (probably) occurs via a chain mechanism and the molecular weights are of the order of  $10^6$ . It is felt by some that the polymerization mechanism is very closely related to the types of reactions the polymer will undergo. (A mechanism is a description of what is occurring on the molecular level; that is, the transfer of atoms and changes in chemical bonding involved in a reaction. A chain mechanism indicates a process in which the products formed help promote the reaction.)

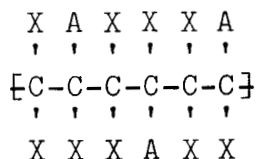
The above discussion has implied a linear addition of monomer units. However, many polymers are known to undergo some branching (non-linear addition) during the polymerization reaction. This branching can result in what is commonly termed cross-linked polymers. It will be shown later that many physical and chemical properties of polymers depend to a large extent on the degree of cross-linking. Furthermore, it is felt that a knowledge and understanding of the molecular structure is necessary in explaining how all polymers behave.

The conditions under which the polymers are prepared can govern properties other than cross-linking. They can lead to certain regularities or irregularities in the chain. There are three types of polymers categorized according to monomer patterns:

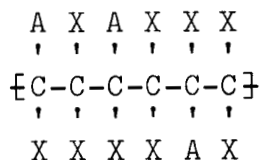
1. Isotactic: stereochemical regularity of structure in the repeating units.



2. Syndiotactic: regular alternation of differences in stereochemical structure in repeating units.



3. Atactic: no regularities to the alternations.



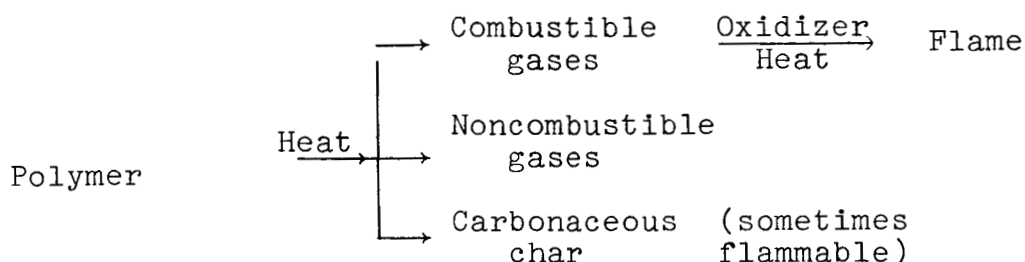
Because of their large size we expect these high molecular weight polymers to exhibit unique properties. Since our major concern is the flammability we shall limit the discussion to thermal stability, pyrolysis, and combustion properties.

## 2. Combustion

The combustion phenomenon has been of interest to scientists for over three hundred years; publications on coal combustion date back to 1667. Despite the years of work devoted to the problem no one has yet been able to develop a general, unified theory which is acceptable to the majority of the scientific and engineering community. A review of even the most simple combustion systems, e.g.,  $H_2$  and  $O_2$ , reveals many voids in understanding arising from various inherent complexities. An awareness of this situation is helpful only in that it leads to the realization that one cannot hope to find simple answers to such questions. This idea should also be extended to the problem of flame propagation. Since the actual combustion is an important

facet of the total propagation picture it can be seen that a thorough understanding of flame propagation can only be achieved after the combustion mechanism itself is well-characterized.

A qualitative scheme of polymer combustion is shown below.



This simple pathway is generally accepted. However, each of the steps indicated involves a very complex series of reactions and only the chemical aspects of the problem have been indicated. Besides understanding the reaction kinetics (i.e., rates of the different chemical reactions involved) we must also include transport phenomena and conservation laws. This involves branching out from chemistry into fluid dynamics thermodynamics, mass transport, and energy exchange.

By individually examining each of the steps in the scheme for polymer combustion we can gain insight into the entire problem and we shall even be able to see that it is possible to build certain desired properties into polymer molecules. This ability has been achieved by slow, stepwise analysis.

First, let us examine what happens to the polymer when it is heated (pyrolysis). Polymers are observed to degrade when they are heated; some break down into the original monomer units and others give a large number of different pyrolysis products. The factors which govern the mode of degradation are the temperature and the atmosphere; but the overriding factor seems to be the nature of the individual polymer. Of all the steps involved in combustion, pyrolysis is probably the most well characterized. Pyrolysis studies have led to an understanding of degradation on a molecular level. Following are a few observations of pyrolytic behavior and some conclusions which can be made.

#### Observations

1. For a given polymer, the pyrolysis products vary with changes in atmosphere and temperature.
2. Most carbon containing chains are not stable above  $\sim 300\text{--}400^\circ\text{C}$  ( $570\text{--}750^\circ\text{F}$ ).

3. Above 500°C (932°F) we must consider the cracking of large chains.
4. When oxygen is present in the chain the thermal stability is usually lowered.
5. Tertiary and quaternary carbons in the chain introduce an element of weakness. (A tertiary carbon atom is one which is bonded to three other carbons; a quaternary carbon is bonded to four other carbons.)
6. High molecular weight favors thermal stability.
7. Cross-linking adds to thermal stability.
8. A double bond is an element of stability in the chain.
9.  $F > H > CH_3 > Cl$ , are observed orders of stability when these different moieties are attached to the chain.
10. Introduction of aromatic groups into the chain enhances the stability. (Aromaticity refers to chemical behavior similar to that of benzene and its derivatives.)

#### Conclusions

1. Pyrolysis products serve as a clue to the mechanism of the thermal degradation.
2. There is more than one mechanism for thermal decomposition.
3. When an oxygen atom replaces carbon in the chain a lowering of stability will occur because the C-O bond is weaker than the C-C bond.
4. The presence of tertiary or quaternary carbon atoms in the chain is not desirable. (Polystyrene  $\left[ \underset{\text{C}_6\text{H}_5}{\text{CH}_2 - \text{CH}_2} \right]_n$  possesses a tertiary carbon, and therefore is not especially heat resistant.)
5. Relative stabilities can be predicted on the basis of different moieties attached to the chain and their decomposition mechanisms. For example, an abundance of hydrogen will result in intramolecular transfer of atoms; but when hydrogen is replaced by bulky alkyl groups the hydrogen transfer will be restricted.

6. The presence of aromatic groups in the chain is desirable. (Kapton, an especially stable film, is synthesized by a polycondensation reaction between an aromatic acid and an aromatic amine.)

Even at this early stage in the discussion it can be seen that by analyzing information derived from pyrolysis studies it is possible to design polymers which will not be highly flammable. It is possible to design polymers which favor formation of an inert char and noncombustible gases, along with a very small volume of combustible gases. It is also possible to design a system which will decompose endothermally rather than exothermally. Also, fillers which promote these desirable properties may be added. Many of these suggestions have been implemented and thermally resistant Kapton and Nomex-nylon are two of the resulting products. However, many desirable properties of the polymers can be destroyed in the process of rendering them non-flammable and quite often toxic decomposition products result. It should also be noted that many of these thermally stable polymers were designed for use in an air atmosphere and in some instances behave quite differently in an oxygen rich atmosphere. It will be pointed out below, however, that our understanding of pyrolysis is far from complete.

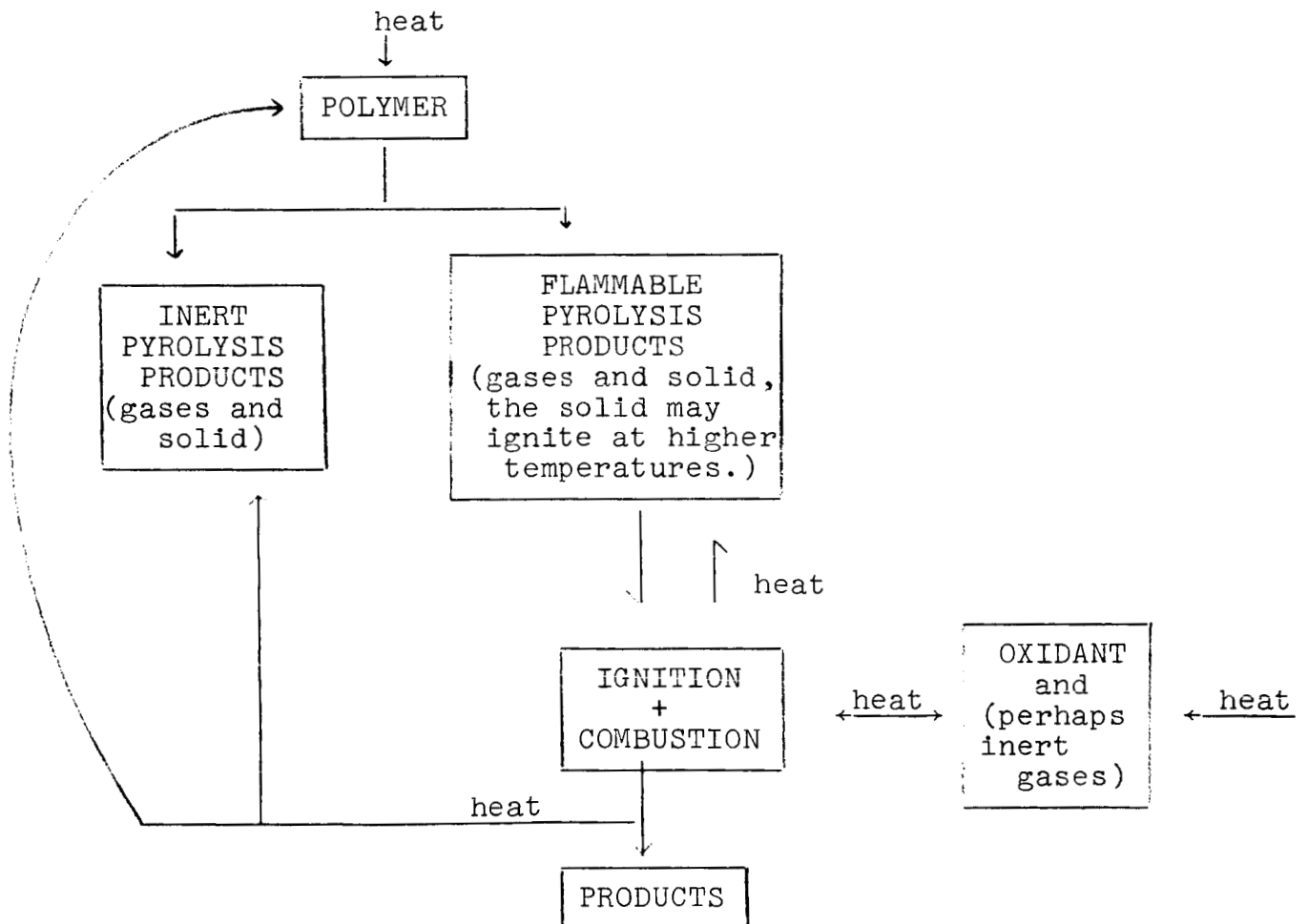
Unfortunately, the understanding of combustion and flame propagation is even less extensive than that of pyrolysis. There are many explanations, some of which are diametrically opposed to one another. In order to illustrate this, some models of combustion and flame propagation will be discussed and compared.

We shall continue to work within the framework of the polymer combustion scheme previously described. This scheme embodies Faraday's original formulation of the distillation (or volatiles) theory of ignition. This theory is supported by photographic experiments which have demonstrated that ignition starts in the volatiles, i.e., ignition was observed at a point above the surface of the solid. This model raises some interesting questions. Are volatiles in the interior formed with as much ease as volatiles at the periphery of the active area? If they are, how can they escape from the center unless and until the material forms many major cracks for them to escape by? (It is suggested that investigators examine the solid residue after combustion and look for any volatiles' escape channels.)

It should also be pointed out that some work has indicated that in fast explosion flames there was probably not time for volatiles to be generated. It is postulated that under these conditions of very rapid heating where volatilization cannot occur the material must burn as solid particles without decomposing. (These two descriptions of pyrolytic behavior can only

lead to the conclusion that the detailed pyrolytic behavior of burning solids is still somewhat obscure. Furthermore, an interesting question is raised: What happens to "thermally stable" polymers when they are subjected to a very rapid temperature increase? Is there a difference in combustion mechanisms which allows polymers which would be flame resistant or self-extinguishing to become combustible? Perhaps a consideration of this possibility could help explain the higher than expected burning rates observed for Nomex and Teflon in pure  $O_2$  at 1 atmosphere, since this atmosphere would probably result in high flame temperatures and very rapid heating.)

Below is a simplified schematic representation of the heat transfer in our combustion model; it should be of help in the discussion which follows:



From this representation we can see that heat is evolved in the combustion process, this heat is then channeled back into the entire system; some is used in initiating further combustion, and the remainder is absorbed by the inert matter which is either initially present or has been produced by the combustion. Therefore, in addition to the chemical reactions we much consider the manner in which heat is absorbed throughout the system. For example, if we consider a polymer which decomposes primarily into combustible gases in an oxygen-rich atmosphere there will be a relatively small concentration of inert matter and most of the heat generated will be used to further the combustion of the reactants. On the other hand, if the pyrolysis products consist of a considerable amount of inert material and the atmosphere contains a large amount of inert matter, this inert matter may act as an effective heat sink and only a small amount of the generated heat will be directed into the reactants. This situation would result in either slow combustion or a self-extinguishing system.

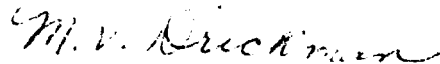
There exists some question as to what the controlling factors in combustion are. Some workers feel that the exothermic chemical reactions are of primary importance; i.e., the critical factor is the rate of heat release and absorption. This approach is sometimes called the chemical or kinetic approach to combustion. It proposes that the principal events take place in the gas phase and that the flame propagation rate is sensitive to variations in oxygen content and total pressure level.

An opposing view assumes that the combustion rate is primarily controlled by the rate of mass transfer of the reactants to the flame, rather than by chemical kinetics. (However, it is conceded that reaction kinetics become important when the volume required for combustion becomes a significant fraction of the available volume.)

Although both approaches stress different rate controlling mechanisms they both agree that the true picture is probably somewhere between the two and that extremes of conditions may favor one mechanism over the other. Both of these approaches will be employed in a future paper which will attempt to analyze some of the existing combustion and flame propagation data. It is hoped that it will be possible to attempt to rationally describe the flame propagation in terms of distance parameters, temperature, concentrations, reaction kinetics, diffusion, convection, and rates of heat release.

## SUMMARY

Some basic definitions and descriptions of polymer behavior have been presented along with a qualitative and simplified picture of combustion and flame propagation. Future papers will extend the theoretical development and attempt to correlate and explain the data. It is hoped that such an appraisal of the data may yield ideas for further worthwhile experimental work. The information presented here is expected to be of help in this endeavor.



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